Chs. Non-ideal behavior

Imperfect gases $\Rightarrow$ Intermolecular forces.

Ideal gas law \[ pV = NkT \]
strictly holds only if molecules do not interact with each other, i.e., for dilute gases. Average distance between neighboring molecules is very large, so that the forces they exert on one another are generally weak.

Ideal gas law is the low-density limit \( (N/V \to 0) \) of a more general gas law in which \( p/kT \) is equal to \( N/V \) to leading order in the small quantity \( N/V \), but in which there are successfully smaller correction terms \( (N/V)^2 \), \( (N/V)^3 \), and so on.

Thus, it is in a sense an expansion in powers of \( N/V \)

\[
\Rightarrow \quad p = \frac{N}{V} \left( 1 + \frac{BN}{V} + \frac{CN}{V^2} + \ldots \right)
\]

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N.B: In practical calculations \( N/V \) is measured in terms of moles per unit volume rather than molecules/volume. Units of \( B \) and \( C \) may differ by factors that are powers of the quagadria number.

Coefficients \( B, C, \ldots \) etc. known as virial coefficients and are temperature dependent as it turns out.

\( B \Rightarrow \) second virial coefficient; \( C \Rightarrow 3^{rd} \) virial coefficient

1 $\Rightarrow$ first virial coefficient.
The form of the general gas law (as described above) and the identity of the virial coefficients can be obtained by looking at the inter-molecular forces.

Most deviations from ideal behavior due to higher densities are those arising from first correction term $B(N)$. For most cases, single correction term $B(N)$ is generally sufficient. Thus, $B(N)$ is the only one of any importance and it is always the most important.

First order correlations, further terms $\Rightarrow$ higher order correlations.

If there were no forces then the virial coefficients would be zero and gas would be ideal.

**Intramolecular forces**

\[ \phi(r) \]

Typical potential energy of interaction $\phi(r)$ between non-bonding atoms or spherical or nearly spherical molecules as a function of distance $r$ between them.

$\phi(r)$ has same form as $V(r)$ potential curve of a covalent molecule but qualitatively different and different in its physical origin.
\( V(r) \) associated with a real typically strong chemical bond. Its depth is a measure of bond strength and position of minimum is the bonding distance.

Depth of \( \phi(r) \) is 100x smaller than for \( V(r) \). Minimum in \( \phi(r) \) is much further out - twice as far or more - than that in \( V(r) \).

e.g. \( V(r) \) \( \rightarrow \) diatomic chlorine interatomic potential.
\( \phi(r) \) \( \rightarrow \) interaction potential of a pair of argon atoms. Ar and Cl nearly equal number of electrons but interaction very different.

For Ar: \( \phi(r) \) determined from heat of vaporization of liquid - or from \( B(r) \) - has a minimum of about 1 kJ/mol. or 0.01 eV/atom pair. Energy of dissociation of \( Ar \) from its ground state vibrational state is 2.5 eV. (Minimum deeper than that by amount \( \approx \) equal to zero-point vibrational energy).

\( r_0 \) for Ar...Ar is \( 3.7 \text{ Å} \), equilibrium internuclear distance in Cl is \( 2.0 \text{ Å} \).

Both \( V(r) \) and \( \phi(r) \) go to zero as \( r \to \infty \) just by convention of the arbitrary zero of potential energy.

Forces of which \( \phi(r) \) is the potential are called van der Waals forces: both attractive and repulsive.

\( r < r_0 \) force \(-d\phi(r)/dr\) is +ve, i.e. repulsive
\[ r > r_0, \quad -dd(r)/dr < 0 \quad \Rightarrow \text{i.e. force of attraction.} \]

Repulsion for \( r < r_0 \) is very strong. Becomes positive at about 0.9\( r_0 \) after which it increases rapidly with decreasing \( r \).

Origin of sudden strong repulsion \( \Rightarrow \) Coulomb repulsion between electrons of two atoms/molecules and Pauli repulsion between electrons of same spin. Repulsion sets in when the two electron clouds begin to interpenetrate and becomes stronger very rapidly with increasing overlap. This distance \( \sigma \) (0.9\( r_0 \)) at which strong repulsion sets in suddenly is a measure of "size" of atom/molecule; \( \sigma \) is twice its radius. Repulsion \( \sigma \) strong that molecules may often be conveniently thought of as infinitely hard sphere-like billiard balls - of diameter \( \sigma \).

\[ \text{\includegraphics{image.png}} \]

Attraction has a different origin. Consider pair of atoms in their (non-degenerate) ground state. Each one has on average a spherically symmetric distribution of electronic charge about its nucleus and so has no permanent dipole moment.

Nevertheless, at any instant, there are momentary imbalances in the electronic charge distribution, hence momentary dipole moments that are not zero.

If atoms close enough to feel each others' presence, slight correlation between directions of instantaneous
A dipole in one atom with that in the other, i.e. at the
instant the dipole in left-hand atom is oriented left to-
right, the right-hand atom is slightly more likely than
not to be oriented in the same direction, for that
produces an energetically favorable change distribution
in which the excess positive charge on one side of one of
the atoms is closest to the excess negative charge on
the other atom. Instantaneous dipole of one atom has
polarized the other atom, the polarization then producing
an attractive dipole-induced-dipole interaction.

Note the polarization is only statistical; the (weak)
correlation between the momentary charge imbalances
on the two atoms produces configurations that are only
slightly more attractive than they are repulsive, resulting
in a (weak) net attractive force (known as London force).

Correlations stronger at shorter distances but become
(rapidly weaker as $r$ increases and disappear at $r\approx\infty$.

Potential energy of Dipole-dipole interactions is proportional to
$1/r^3$ but since London forces only a correlation effect
they appear only as a second-order perturbation.\(^{10}\)
vanishes proportionally to $1/r^6$ at large $r$.
(For molecules with permanent dipoles, also $1/r^6$
dependence due to thermal averaging over orientations.
In correlation-based London forces, averaging is
electronic.)
An empirical representation of $\phi(r)$ in analytic form:

$$\phi(r) = \varepsilon \left( \left( \frac{r_0}{r} \right)^1 - 2 \left( \frac{r_0}{r} \right)^{6} \right)$$

known as the Lennard-Jones potential.

large $r \gg 1/r^6$ term vanishes more slowly than $1/r^{12}$
.: $\phi(r)$ vanishes proportionally to $1/r^6$ and does so through
$-\varepsilon$ values

small $r \ll 1/r^{12}$ term goes to $\infty$ more rapidly than $1/r^6$
term . $\phi(r)$ goes to $\infty$ at a very rapid pace. This is
realistic but exact $1/r^{12}$ form of dependence is empirical
(not always very accurate).

Minimum in $\phi(r)$ is when $d\phi(r)/dr = 0$

$$-12 \left( \frac{r_0}{r} \right)^{12} \frac{1}{r^{13}} + 12 \frac{r_0^6}{r^7} = 0$$

.: $r = r_0$ is point where $\phi(r) \Rightarrow$ minimum
and $\phi(r) = -\varepsilon$ at this point.

$\phi(r)$ crosses r-axis at $r = 2^{-1/6} r_0 = 0.89 r_0$
$\sigma$ is often considered the molecular diameter.

Another form of $\phi(r) \Rightarrow$ square-well potential

\[ \phi(r) \]

\[ 0 \]

\[ \sigma_1 \]

\[ \sigma_2 \]

\[ r \]

\[ -\varepsilon \]
\[ \phi(r) = \begin{cases} \infty & r < \sigma_1 \\ -\infty & \sigma_1 < r < \sigma_2 \\ 0 & r > \sigma_2 \end{cases} \]

This gives strong repulsion - infinitely sudden and infinitely strong at small distances.
attraction at intermediate distances - flat.
At larger distances, interaction falls off more-or-less rapidly.
even the idealized square-well potential also proves adequate to account for form & temperature dependence of \( B(T) \) when \( \sigma_2 \approx 1.5 \sigma_1 \) (width of square-well potential is \( \approx 0.5 \) molecule's hard-sphere diameter).

\( B(T), C(T), \ldots \) etc. can be obtained from \( \phi(r) \):
If \( \phi(r) = 0 \) at all \( r \), gas \( \rightarrow \) ideal & \( B(T), C(T), \ldots = 0 \) at all \( T \).

Molecule at some point \( O \) in the volume. What is average density at any point such as \( P \), distant \( r \) from \( O \)?

If \( \rho = \frac{N}{V} \) is overall avg number density in the gas then the mean density at \( P \) given that there is a molecule at \( O \) would differ from \( \rho \) by some factor, call it \( g(r) \) - that takes into account correlations in the distribution of molecules arising from forces they exert on each other.
mean local density at distance from $r = \rho g(r)$.

Function $g(r)$ is the radial distribution function or pair distribution function and plays an important role in the theory of the liquid state as well as that of the ideal gas.

**Form of $g(r)$**

- **Dilute gas**: $g(r)$ takes into account potential energy $\phi(r)$ that a molecule at $P$ feels due to the presence of a molecule at $O$. From Boltzmann distribution law, we get
  \[ g(r) = e^{-\frac{\phi(r)}{kT}} \]

  (More correctly, $g(r) = e^{-\frac{\phi(r) - \phi(0)}{kT}}$ but as per convention $\phi(0) = 0$).

For $\phi(r) = 0$ $\Rightarrow$ molecules do not exert forces on one another $\Rightarrow g(r) = 1$ at all $r$.

This means density at $P$ $\Rightarrow$ $\rho$, mean overall density.

Presence of a molecule at $O$ would exert no influence on the presence or absence of any other molecule at any distance from $O$ and gas would be ideal.

However, when $\phi(r)$ non-zero, attractions and repulsions between molecules make local density different from overall $\rho$. At large enough distances, however, forces between molecules are so weak that these
Correlations are lost, i.e. \( g(\infty) = 1 \).

\[
g(r)
\]

Because of strong repulsion between molecules at close approach, it is very unlikely that another molecule will be found very close to a given molecule at \( 0 \). The mean local density at small \( r \) must be much less than the overall \( \rho \), i.e., \( g(r) \) must be much less than 1 at small \( r \).

Molecules attract each other at intermediate \( r \), so a larger number of molecules than average will be found at such distances from molecule at \( 0 \). i.e. at such distances \( g(r) \) must exceed 1.

At large \( r \), \( g(r) \) goes to 1: \( \phi(r) \to 0 \) as \( r \to \infty \). Thus density at large distances from \( 0 \) is same as average density.

This is all true if gas is dilute, when only correlating effect at \( P \) due to molecule at \( 0 \) is through direct action of potential \( \phi(r) \). If gas is not too dilute, \( g(r) \) would be more complicated and we have to account for fact that molecules attracted to or repelled by molecule at \( 0 \) also attract and repel each other (higher-order correlations).
Thus the \( g(r) \) needs to include corrections as a series in increasing powers of the density \( \rho = N/V \), each successive term being a more refined correction to the preceding. Thus,

\[
g(r) = e^{-\Phi(r)/kT} + pg_1(r) + \rho^2 g_2(r) + \ldots
\]

\( g_1, g_2 \) may depend on \( T \) in addition to \( r \) but not on \( \rho \). That dependence comes only in the powers \( \rho, \rho^2, \ldots \) etc.

For \( B(r) \), these corrections are not needed. A low-density approximation to \( g(r) \) is sufficient.

For \( c(r) \) \( \Rightarrow \) first correction \( pg_1(r) \) needed
For \( h(r) \) \( \Rightarrow \) both \( pg_1(r) \) and \( \rho^2 g_2(r) \) needed as correction

With each correction, \( g(r) \) becomes increasingly complex. It develops a series of maxima and minima.

Even in liquids, some features of simple \( g(r) \) persist. For small \( r \), \( g(r) \) remains vanishingly small, has a prominent peak at intermediate \( r \), followed by a succession of subsidiary peaks and valleys and ultimately approaches 1 as \( r \rightarrow \infty \).